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(19) (CA) **CANADIAN PATENT** (12)

(54) Application of a Painted Carrier Film to a
Three-Dimensional Substrate

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Application of a painted carrier film to a three-dimensional substrate

Abstract of the Disclosure

A carrier film is coated on one side with a radiation curable paint and on the other with an adhesive. The paint is cured by irradiation, the carrier film is heated and, in the thermoplastic state, applied to a three-dimensional substrate. The paint can also be cured in two steps by first irradiating and then heat curing it.

A-17241/+Application of a painted carrier film to a three-dimensional substrate

The present invention relates to a method of applying a painted carrier film to a three-dimensional substrate, especially the step of applying the paint to said carrier film.

10 A method of coating automobile panels with a painted carrier film is disclosed in European patent application 0 251 546 (published January 7, 1988). This method consists in coating one side of the carrier film with a pigmented paint, which is heat cured. The other side of the carrier film is coated with an adhesive which can be heat activated. The carrier film so coated with paint and adhesive is then heated until it is sufficiently soft for deep drawing. The hot film is then applied to the automobile panel under vacuum, such that the adhesive binds the film permanently to said panel. Compared with the conventional method of painting, this method has the advantage of being technologically simpler and of ensuring a uniform thickness of the coating over the entire area of the three-dimensional substrate.

20 A particular difficulty of this method resides in the heat curing of the paint on the carrier film. In the required curing temperature range (ca. 120-150°C), many carrier films soften and, in the process, lose their shape. For this reason, only films which are resistant to high temperature can be used, and this in turn requires high temperatures for the later step of heating the carrier film until it is soft.

It has now been found that the curing of the paint can be effected at room temperature and in a short time by using as paint a radiation curable paint and by partially or completely curing said paint on the carrier film by irradiation.



Accordingly, the present invention provides a method of applying a painted carrier film to a three dimensional substrate of solid material, which carrier film is first coated on a top side with a paint and on an underside with an adhesive, and then heating said carrier film and applying it, while hot, with the adhesive coated side to said substrate, wherein the paint used is a radiation curable paint which is cured in a first step after application to the carrier film, prior to the application to the substrate into a tack-free thermoplastic state by irradiation and is heat-crosslinked in a second step after application of the carrier film to the substrate.

Irradiation may be effected with, for example, UV light or electronic beams or visible light. Irradiation is preferably effected with UV light.

The carrier film employed is preferably one made from a thermoplastic material, for example from polyethylene, polypropylene, polyvinyl chloride, polyurethane, polyester, polyamide or polyethylene terephthalate. The thickness of the carrier film is conveniently not less than 20 μm . The carrier film can be pigmented, but is preferably transparent. The carrier film may contain stabilisers, for example antioxidants, light stabilisers, processing auxiliaries, metal passivators, thiosynergists, phosphites or metal carboxylates. It may contain the further modifiers commonly used in films, for example fillers, lubricants, antistatic agents or plasticisers. The film can be provided with a surface treatment, for example with an oxidising agent, by flame treatment or by corona discharge. Such surface treatment effects a better adhesion of

the paint and of the adhesive. The carrier film can be oriented by drawing in one or two directions.

The radiation curable paint is based on a binder which is either radically or cationically polymerisable, or is radically as well as cationically polymerisable, or which can be cured by acid catalysis. Normally the binder consists of a mixture of radiation curable compounds which are curable by means of the same or different mechanisms. Depending on the mechanism by means of which the binder can be cured, appropriate curing catalysts (photoinitiators) are used.

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The radically polymerisable binders are ethylenically unsaturated compounds. They are mono- or polyunsaturated compounds, the latter being of especial importance, as they can be polymerised to crosslinked - and hence insoluble - products.

10 Illustrative examples of monounsaturated compounds are acrylates or methacrylates of monohydric alcohols, acrylamides and similar acrylic acid derivatives, for example methyl acrylate, ethyl acrylate, butyl acrylate, isooctyl acrylate or hydroxyethyl acrylate, methyl or ethyl methacrylate, acrylonitrile, acrylamide, N-butyl(methacrylamide); as well
as vinyl and allyl compounds such as vinyl acetate, vinyl stearate, N-vinyl pyrrolidone, vinylidene chloride, vinyl benzene or allyl acetate.

20 Typical polyunsaturated compounds are acrylates, methacrylates or itaconates of polyols such as ethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, butanediol-1,4-acrylate, propanediol-1,2-diacrylate, butanediol-1,3-dimethacrylate, neopentyl glycol diacrylate, trimethylolpropane di(meth)acrylate, trimethylolthane di(meth)acrylate, glycerol di- and triacrylate, pentaerythritol di-, tri- and tetraacrylate or pentaerythritol di-, tri- and tetramethacrylate, dipentaerythritol tetra-, penta- and hexaacrylate,
30 dipentaerythritol tetra-, penta- and hexamethacrylate or dipentaerythritol tetra-, penta- or hexaitaconate, sorbitol tetraacrylate, sorbitol hexamethacrylate, diacrylates or dimethacrylates of 1,4-cyclohexanediol, 1,4-dimethylolcyclohexane, 2,2-bis(hydroxyphenyl)propane; of polyethylene glycols or of oligoesters or oligourethanes having hydroxyl end groups. Suitable polyunsaturated monomers which may also be used are acrylamides such as methylene bis(acrylamide), hexamethylene-1,6-bis-(acrylamide), diethylenetriamine tris(methacrylamide), bis(methacrylamidopropoxy)ethane or 2-acrylamidoethyl acrylate. Examples of poly-
unsaturated vinyl and allyl compounds are divinyl benzene, ethylene glycol divinyl ether, diallyl phthalate, allyl methacrylate, diallyl maleate, trisallylisocyanurate or triallyl phosphate.

Polymeric or oligomeric polyunsaturated compounds can also be photopolymerised to crosslinked products, for example unsaturated polyesters and copolyesters of maleic acid and fumaric acid, (meth)acrylates of

polyvinyl alcohol or homopolymers or copolymers of butadiene or isoprene. Further useful unsaturated components are the reaction products of polyepoxides with acrylic or methacrylic acids. Suitable polyepoxides are mainly the epoxy resin precursors which are commercially available and obtainable in different molecular weights.

- 10 Mixtures of such unsaturated compounds are normally used for the photopolymerisation so as to be able to vary the properties of the polymers for the desired end use. Exemplary of such mixtures are mixtures of diacrylates with polyester acrylates or with polyurethane acrylates, mixtures of mono-, di- and triacrylates, mixtures of unsaturated polyesters of maleic acid with styrene or other mixtures of polymeric-oligomeric unsaturated compounds with di- tri- or tetraacrylates. The mixtures may consist of two, three or more unsaturated components.

- 20 Suitable photoinitiators for radically polymerisable binders are in particular aromatic carbonyl compounds. Examples of such photoinitiators are benzoin, benzil, benzophenone, the benzoin alkyl ethers, the esters of phenylglyoxylic acid, α -trichloroacetophenone, α -diethoxyacetophenone, benzil dimethyl ketal, 1-benzoylcyclohexanone, the α -hydroxyacetophenones disclosed in German Offenlegungsschrift 2 722 264 (published November 23, 1987), the α -aminoacetophenones disclosed in European patent application 0 88 050 (published September 7, 1982), 0 117 233 (published August 29, 1984) or 0 138 754 (published April 24, 1985), as well as the aroyl-phosphine oxides disclosed in European patent application 0 7508 (published February 6, 1980) or 0 40 721 (published December 2 1981). These compounds are so-called α -cleavers. When subjected to radiation, they decompose into radical fission products which initiate the polymerisation of the unsaturated compounds. They are often also used in conjunction with amines such as triethanolamine, N-methyldiethanolamine, p-dimethylaminobenzoate or Michler's ketone.

- 30 Together with the photoinitiators it is also possible to use sensitisers which sensitise the photocurable system for specific wavelength ranges. Illustrative of such sensitisers are thioxanthone, anthracene and coumarin derivatives.
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Thermal initiators such as benzoyl peroxide, cyclohexanone peroxide or methyl ethyl ketone peroxide may also be used together with the photo-initiators.

Cationically polymerisable binders are specific ethylenically unsaturated compounds such as isobutylene, styrene, N-vinylpyrrolidone, isoprene, butadiene, alkyl vinyl ethers or vinyl esters, or heterocyclic compounds, preferably 3- and 4-membered heterocycles such as alkylene oxides, epichlorohydrin, glycidyl ethers, glycidyl esters, epoxy resins, oxetanes, dioxolanes, trioxane, lactones, thiiranes, thietanes or azetidines.

Particularly important cationically polymerisable binders are epoxy resins, especially the diepoxides and polyepoxides and epoxy resin prepolymers of the kind used to prepare crosslinked epoxy resins. The diepoxides and polyepoxides may be aliphatic, cycloaliphatic or aromatic compounds. Illustrative of such compounds are the glycidyl ethers and 8-methyl glycidyl ethers of aliphatic or cycloaliphatic diols or polyols, for example those of ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, diethylene glycol, polyethylene glycol, polypropylene glycol, glycerol, trimethylolpropane or 1,4-dimethylolcyclohexane or of 2,2-bis(hydroxycyclohexyl)propane and N,N-bis(2-hydroxyethyl)aniline; the glycidyl ethers of diphenols and polyphenols, for example resorcinol, 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenyl-2,2-propane, novolaks and 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane. Further examples are N-glycidyl compounds such as the diglycidyl compounds of ethyleneurea, 1,3-propyleneurea or 5-dimethylhydantoin or of 4,4'-methylene-5,5'-tetramethyldihydantoin, or those such as triglycidyl isocyanurate.

Further glycidyl compounds of technical importance are the glycidyl esters of carboxylic acids, especially dicarboxylic and polycarboxylic acids, for example the glycidyl esters of succinic acid, adipic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, tetra- and hexahydrophthalic acid, isophthalic acid or trimellitic acid, or of dimerised fatty acids.

Examples of polyepoxides different from glycidyl compounds are the diepoxides of vinyl cyclohexane and dicyclopentadiene, 3-(3'-epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro[5.5]undecane, the 3',4'-epoxycyclohexyl-methyl ester of 3,4-epoxycyclohexanecarboxylic acid, butadiene diepoxide or isoprene diepoxide, epoxidised linoleic acid derivatives or epoxidised polybutadiene.

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Particularly suitable photoinitiators for cationically curable binders are the aromatic sulfonic and iodonium salts disclosed in US patent specifications 4 058 401, 4 069 054 or 4 394 403. Further initiators are the arene cyclopentadienyliron(II) salts disclosed in European patent application 0 94 915 (published November 23, 1983).

These cationic photoinitiators too can be used in conjunction with a sensitiser, as described in European patent application 0 152 377 (published August 21, 1985). In conjunction with oxidising agents, especially with peroxide compounds, the iron(II) salts mentioned above can be used for cationic as well as for radical photocuring as taught in European patent application 0 126 712 (published November 28, 1984).

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With the aid of the iron(II) complex salts it is also possible to effect the radiation curing of two-component polyurethanes as taught in European patent application 0 250 364 (published December 23, 1987). The polyurethanes are formed from a polyol and a polyisocyanate. The polyol is preferably a hydroxyl group containing acrylic or epoxy resins. A blocked polyisocyanate can also be used as polyisocyanate.

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Binders which can be cured by acid catalysis may be radiation cured if the initiator used is a compound which generates an acid when irradiated. Examples of such curable binders are specific alkyd resins, acrylic resins, polyester resins, melamine resins, urea resins, phenolic resins and mixtures thereof, especially the mixtures of alkyd, acrylic and polyester resins with melamine resins. In particular they are etherified melamine resins which are used for acid-curable paints. The polymerisation is carried out, when using these resins, not by addition polymerisation but by polycondensation. The photoinitiators used for such systems are compounds which generate an acid when irradiated. Examples of such

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photoinitiators are the benzoin sulfonates disclosed in European patent application 0 84 515 (published July 27, 1983) or 0 89 922 (published September 28, 1983), or the oxime sulfates disclosed in European patent application 0 139 609 (published May 2, 1985).

10 Particularly useful binders are hybrid systems. These are mixtures of radically or cationically curable and acid-catalysed curable compounds which contain a radical or cationic photoinitiator as well as an acid-generating photoinitiator. Irradiation of such hybrid systems effects initially only the polymerisation of the radically or cationically curable component and the generation of the acid from the acid catalyst. Subsequent heating of the system induces the polycondensation of the acid-curable component. Mixtures of hydroxyl group containing acrylates and melamine resins are exemplary of such hybrid systems. Linear polyacrylates are formed in the first (radical) curing step and are cross-linked in the second (thermal) curing step by the melamine resin.

All these types of photocurable binders are either mixed with a pigment or they are used unpigmented as clear coating. Suitable pigments are all customary inorganic, organic or metallic pigments.

20 The paints may contain light stabilisers, for example UV absorbers from the class of the benzotriazoles, benzophenones or oxanilides, but preferably sterically hindered amines (HALS), for example derivatives of 2,2,6,6-tetramethylpiperidine. Further ingredients which may be added to the paint are antioxidants, levelling agents, couplers or thixotropic agents. For application, the paint may be diluted with solvent, but it is preferred to use a solvent-free paint.

30 The paint is applied to the top side of the carrier film in a thin layer, using conventional techniques of applying paints, for example brushing, knife-coating, casting, extruding, roll coating or spraying. If a solvent is used, then it is allowed to evaporate substantially after application of the paint. This drying can be accelerated by gentle heating (for example by infrared irradiation). The paint is then irradiated with energy-rich sources of radiation. Such sources are suitably in particular UV radiants such as mercury low-pressure, medium-pressure or high-pressure lamps, xenon lamps, argon lamps or metal halide lamps. The light

of these lamps is rich in short-wave light having a wavelength in the range of 200-600 nm. Laser beams are also suitable, as are also electron beams.

The paint can also be applied in two layers. For example, it is possible first to apply a pigmented paint and then over it a coat of clear paint which contains a light stabiliser. The radiation curing of the two layers can be effected individually or jointly.

10 A complete cure (crosslinking) of the paint is not necessary when effecting the radiation curing. The paint need only be cured to such a degree that it has a wipe-resistant finish. Further curing can be effected when the carrier film is later heated.

In a special embodiment of the method of this invention, the paint is converted by irradiation into a thermoplastic state after application to the carrier film (precured) and heat-crosslinked (postcured) after application of the carrier film to the substrate. The heat-crosslinking is preferably carried out by heating to 100-160°C.

20 The underside of the carrier film is coated with an adhesive. This can be done before or after application of the paint. The adhesive can be, for example, a hot melt adhesive which is solid at normal temperature. It can be applied to the carrier film from solution or from the melt, and is dried or allowed to cool on the carrier film.

The adhesive may also be a contact adhesive which is soft and adhesive at room temperature. In this case, the carrier film is provided with an anti-adhesive protective backing after application of the adhesive (from solution or in the melt), which backing is stripped off before the carrier film is applied to the three-dimensional substrate.

30 It is also possible to apply precursors (monomers, oligomers) from which a (polymeric) adhesive is formed by irradiation with UV light or electron beams. The adhesive can therefore also be a material which can be cured or activated by radiation.

Before application to the three dimensional substrate, the carrier film coated on the top side with paint and on the underside with adhesive is plastified. The adhesive can also be activated by this procedure, and activation can also be completed by the curing of the paint.

10 The plastified carrier film is applied to the three-dimensional substrate. Firm adhesion to the substrate can be effected by applying a vacuum to the carrier film as described in European patent application 0 251 546, or the carrier film is pressed on to the substrate by pressure, for example by means of a suitably shaped press. The side of the carrier film coated with adhesive can also be bonded to the substrate by the action of electron beams.

The substrate to be coated can be made of any solid material, especially of metal, plastic, wood, glass or ceramics material. Examples of such substrates are automobile body parts or claddings of domestic appliances made of metal or plastic, or furniture or furniture parts made of wood.

The following Examples illustrate in detail how the method can be performed. Parts and percentages are by weight, unless otherwise stated.

Example 1: A photocurable paint is prepared by mixing the following ingredients:

- 20 55 parts of a urethane acrylate (Ebecryl® 284, UCB),
14 parts of hexanediol diacrylate,
14 parts of trimethylolpropane triacrylate,
12 parts of polyethylene glycol diacrylate (Sartomer® 344, ARCO),
4 parts of a radical photoinitiator (Irgacure® 184, Ciba-Geigy).

The paint is cast in a continuous process on a 200 µm thick film of thermoplastic polyester and, at a speed of 10 m/min, is cured to a 30 µm film under two 80 W/cm mercury medium-pressure lamps positioned diagonally to the web of polyester film. The painted film is turped by guide rolls such that, in a subsequent step, a hot melt adhesive can be cast

hot on the non-painted side of the film. When the hot melt adhesive has cooled, the film, which is now non-tacky on both sides, is wound on to a roll and stored for further use.

10 The treated carrier film is used for coating a metal automobile body part. The procedure is that, first, a sufficiently large segment of the film is clamped into a frame and placed over a vacuum chamber such that the adhesive-coated side of the carrier film and the side of the automobile part to be coated are adjacent. The carrier film is then plastified by heating with hot air to ca. 130°C, whereupon the adhesive is also activated, i.e. melted. The hot carrier film is deep drawn by evacuating the air present in the vacuum chamber and applied to the automobile part. When the adhesive has cooled, the carrier film is firmly and permanently bonded to the automobile part.

Example 2: A hybrid system is prepared by mixing a radically photocurable component A comprising:

60 parts of a urethane acrylate (Ebecryl® 284, UCB),
25 parts of hydroxyethyl acrylate,
8 parts of ethoxyethoxyethyl acrylate (Sartomer® 256, ARCO),
7 parts of 2-hydroxyethyl methacrylate,
20 6 parts of a radical photoinitiator (Irgacure® 184, Ciba-Geigy),

and a component B which can be cured by the catalytic action of a photodeblockable acid and which comprises:

25 parts of an alkylated melamine resin (Cymel® 303, American Cyanamide),
75 parts of an acrylic polyol (Paraloid® AT 400, Rohm),
6 parts of a photodeblockable acid catalyst (2-oxo-1,2-diphenylethyl-p-dodecylbenzenesulfonate)

in the ratio 1:1.

30 The paint is cast in a continuous process on a 200 µm thick film of polyvinyl chloride and, at a speed of 10 m/min, is polymerised to a 30 µm thermoplastic film under four pairs of 80 W/cm mercury medium-pressure

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lamps positioned at intervals of 2 metres diagonally to the web of polyester film. The painted film is turned by guide rolls such that, in a subsequent step, a hot melt adhesive can also be applied by casting. When the hot melt adhesive has cooled, the film, which is now non-tacky on both sides, is wound on to a roll and stored for further use.

10 The treated carrier film is used for coating a metal automobile body part. The procedure is that, first, a sufficiently large segment of the film is clamped into a frame and placed over a vacuum chamber such that the adhesive-coated side of the carrier film and the side of the automobile part to be coated, which is present in the vacuum chamber, are adjacent. The carrier film is then plastified by heating with hot air to ca. 160°C, whereupon the adhesive is activated, i.e. melted. The hot carrier film is deep drawn by evacuating the air present in the vacuum chamber and applied to the automobile part. The automobile part coated with the carrier film is then further heated for 10 to 20 minutes with hot air of ca. 150°C, whereupon a spatial crosslinking and thus complete curing of the paint film takes place through the action of the acid catalyst released in the course of the UV irradiation. When the adhesive has cooled, the painted film is firmly and permanently bonded to the automobile part. A paint cured for 20 minutes at 150°C has a pendulum hardness according to Koenig of 162 seconds (measured on glass).

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of applying a painted carrier film to a three dimensional substrate of solid material, which carrier film is first coated on a top side with a paint and on an underside with an adhesive, and then heating said carrier film and applying it, while hot, with the adhesive coated side to said substrate, wherein the paint used is a radiation curable paint which is cured in a first step after application to the carrier film, prior to the application to the substrate into a tack-free thermoplastic state by irradiation and is heat-crosslinked in a second step after application of the carrier film to the substrate.
2. A method according to claim 1, wherein irradiation is effected with UV light or electron beams or with visible light.
3. A method according to claim 2, wherein irradiation is effected with UV light.
4. A method according to claim 1, wherein the paint is based on a radically polymerisable binder.
5. A method according to claim 1, wherein the paint is based on a cationically polymerisable binder.
6. A method according to claim 1, wherein the paint is based on an acid-curable binder.
7. A method according to claim 1, wherein the paint is applied in two layers.
8. A method according to claim 1, wherein the paint contains at least one photoinitiator.
9. A method according to claim 1, wherein the paint contains a light stabiliser.

10. A method according to claim 1, wherein the heat-crosslinking is carried out in the temperature range from 100 to 160°C.
11. A method according to claim 1, wherein the three-dimensional substrate is of metal, plastic, wood, glass or ceramics material.
12. A method according to claim 11, wherein the substrate is an automobile body part and consists of metal or plastics material.
13. A method according to claim 1, wherein the adhesive is a material which can be cured or activated by irradiation.

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PATENT AGENTS

